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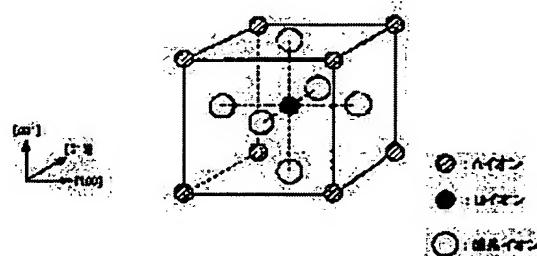
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## (54) DOMAIN CONTROL PIEZOELECTRIC SINGLE CRYSTAL ELEMENT AND ITS MANUFACTURING METHOD

### (57) Abstract:

**PROBLEM TO BE SOLVED:** To provide a domain control piezoelectric single crystal element wherein lateral direction vibration mode ( $k_{31}$ ) is used in which  $k_{31}$  is used effectively in the state that  $d_{33}$  is at least 800 pC/N when  $k_{33}$  is at least 80%, and  $-d_{31}$  is at least 1200 pC/N when  $k_{31}$  is at least 70%, and to provide a domain control piezoelectric single crystal element using a longitudinal vibration mode ( $k_{33}$ ) of high efficiency and high performance wherein spurious or the like is not present in a band width in which  $k_{33}$  vibration mode is used in the condition that  $d_{33}$  is at least 800 pC/N when  $k_{33}$  is at least 80%, and  $k_{31}$  is at most 30%.



**SOLUTION:** As a polarization condition in a thickness direction of a piezoelectric single crystal element, a DC electric field of 400-500 V/mm is applied for at most two hours in a temperature range of 20-200°C, or cooling is performed while an electric field is applied (electric field cooling). As a pre-stage of the above process, an electric field is applied to a direction perpendicular to a polarization direction (electric field application), or temperature is increased and decreased by setting a rhomboidal-tetragonal phase boundary temperature or a tetragonal-cubic phase boundary

temperature as a center temperature, or temperature is increased and decreased between different two temperatures in a cubic system temperature region (thermal treatment), or these temperature operations are used together.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] In the piezo-electric single crystal ingredient which is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$  electromechanical coupling coefficient  $k_{31} \geq 70\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization -- and It has piezo-electric distorted constant  $d_{31} \geq 1200 \text{ pC/N}$ . And the domain control piezo-electricity single crystal component characterized by being value  $f_{c31} \leq 650 \text{ Hz-m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=fr-L$ ) which is the product of the oscillating lay length (L) of a component.

[Claim 2] In the piezo-electric single crystal ingredient which is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$  electromechanical coupling coefficient  $k_{31} \leq 30\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization -- and It has piezo-electric distorted constant  $d_{31} \leq 300 \text{ pC/N}$ . And the domain control piezo-electricity single crystal component characterized by being value  $f_{c31} \geq 800 \text{ Hz-m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=fr-L$ ) which is the product of the oscillating lay length (L) of a component.

[Claim 3] The domain control piezo electric crystal single crystal component according to claim 1 or 2 to which a piezo-electric single crystal ingredient is characterized by being following (a) or (b).

(a) It is the solid solution which consists of  $X\text{-Pb}(A_1, A_2, \dots, B_1, B_2\dots)\text{O}_3+(1-X)\text{PbTiO}_3$  ( $0 < X < 1$ ). 1 or two or more elements which were chosen from the group which  $A_1$ ,  $A_2$ , and  $\dots$  become from Zn, Mg, nickel, Lu, In, and Sc,  $B_1$ , and  $B_2\dots$  are 1 or two or more elements which were chosen from the group which consists of Nb, Ta, Mo, and W. The percentage in  $a_1$ ,  $a_2 \dots$ , and a chemical formula for the ionic valency of  $A_1$ ,  $A_2$ , and  $\dots$ , respectively  $Y_1$ ,  $Y_2 \dots$ ,  $B_1$ ,  $B_2 \dots$  The percentage in  $b_1$ ,  $b_2 \dots$ , and a chemical formula for ionic valency, respectively  $Z_1$ ,  $Z_2 \dots$ , The total W of the ionic valency of the element group in a parenthesis [ in / when it carries out / chemical formula  $\text{Pb}(A_1Y_1a_1, A_2Y_2a_2, \dots, B_1Z_1b_1, \text{and } B_2Z_2b_2\dots)\text{O}_3$  ] is  $W=a_1\text{and } Y_1+a_2Y_2+\dots b_1\text{and } Z_1+b_2Z_2+\dots$  Fill the charge of =4+.

(b) Do 0.5 ppm-1 mass % addition of 1 of Mn and Cr\*\*, or two sorts at the above (a).

[Claim 4] The manufacture approach of the piezo-electric single crystal component characterized by performing the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field as polarization conditions for the thickness direction of a piezo-electric single crystal component, and manufacturing a domain control piezo-electricity single crystal component.

[Claim 5] The manufacture approach of the piezo-electric single crystal component according to claim 4 characterized by manufacturing a domain control piezo electric crystal single crystal component by performing the process which impresses electric field in the direction which intersects perpendicularly in the direction of polarization of a single crystal piezoelectric device as a preceding

paragraph story of a process according to claim 4, performing the process which controls the direction of the ferroelectric domain of the direction which intersects perpendicularly in the direction of polarization, and performing the process subsequently to claim 4 indicated.

[Claim 6] The process which carries out heating cooling of the single crystal piezoelectric device as a preceding paragraph story of a process according to claim 4 on both sides of the transition temperature of rhombohedral [ which is the hypothermic phase of this piezo-electric single crystal ingredient ], and \*\*\*\*\* which is a moderate temperature phase (1), Or the process which carries out heating cooling on both sides of the Curie temperature which is \*\*\*\*\* of this piezo-electric single crystal ingredient, a ferroelectricity, and piezoelectric disappearance temperature (2), Or the process which carries out heating cooling in the cubic temperature requirement which is a parent phase more than Curie temperature (3), Or by performing the process (4) which combined suitably said process (1), (2), and (3), and performing the process subsequently to claim 4 indicated The manufacture approach of the piezo-electric single crystal component characterized by controlling the direction of the ferroelectric domain of the direction which intersects perpendicularly in the direction of polarization, and manufacturing a domain control piezo electric crystal single crystal component.

[Claim 7] The process which impresses electric field in the direction which intersects perpendicularly in the direction of polarization of a single crystal piezoelectric device, The process which carries out heating cooling of the single crystal piezoelectric device on both sides of the transition temperature of rhombohedral [ which is the hypothermic phase of this piezo-electric single crystal ingredient ], and \*\*\*\*\* which is a moderate temperature phase (1), Or the process which carries out heating cooling on both sides of the Curie temperature which is \*\*\*\*\* of this piezo-electric single crystal ingredient, a ferroelectricity, and piezoelectric disappearance temperature (2), Or the process which carries out heating cooling in the temperature requirement of the cube article which is a parent phase more than Curie temperature (3), Or the process which uses together the process (4) which combined suitably said process (1), (2), and (3) is performed. Subsequently, the process cooled impressing 400v/mm - 1500v [/mm ] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field is performed. The manufacture approach of the piezo-electric single crystal component characterized by controlling the direction of the ferroelectric domain of the direction which intersects perpendicularly in the direction of polarization, and manufacturing a domain control piezo electric crystal single crystal component.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to a piezo-electric single crystal component and its manufacture approach. In more detail, it is the component which consists of a single crystal ingredient, and is related with the component which paid its attention to the domain control of the direction which intersects perpendicularly in the direction of polarization, i.e., the electromechanical coupling coefficient of the longitudinal direction oscillation mode and this direction, and its manufacture approach.

**[0002]**

[Description of the Prior Art] About the piezo-electric single crystal component, the ultrasonic probe using the piezo electric crystal which consists of a dissolution single crystal of zinc niobic acid-lead titanate is indicated by JP,6-38963,A, for example. This technique has [ such a piezo electric crystal ] the electromechanical coupling coefficient ( $k_{33}$ ) of the direction of polarization as large as 80 - 85%, and by using this single crystal shows that a highly sensitive probe is obtained. Although a piezo-electric single crystal component is studied about the electromechanical coupling coefficient of the direction of polarization in this way and from Seki also of various kinds of applications is carried out conventionally, about the property of the direction which intersects perpendicularly in the direction of polarization, it is an uncivilized technical field.

**[0003]**

[Problem(s) to be Solved by the Invention] various applications are presented with this invention persons when the electromechanical coupling coefficient ( $k_{33}$ ) of the direction of polarization of a piezo-electric single crystal component (lengthwise direction oscillation mode) has a  $\geq 80\%$  value -- \*\*\*\* -- nevertheless the electromechanical coupling coefficient ( $k_{31}$ ) of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization -- for example IEEE Proc.MEDICAL As shown in the reference of IMAGING3664(1999) pp.239 or others, as compared with the electromechanical coupling coefficient ( $k_{33}$ ) of 49% - 62% and the direction of polarization (lengthwise direction oscillation mode), it is a low value. And it noted that the value which has dispersion with reference was shown. And as a result of inquiring wholeheartedly, for 800 or more pC/N and  $k_{31}$ ,  $-d_{31}^{**}$  is [  $d_{33}$  ] 1200 pC/N (the definition top  $d_{31}$ ) to coincidence at 70% or more simultaneous [  $k_{33}$  ] at 80% or more. More than it had a negative value, when it carries out, manufacture of the piezo-electric single crystal component which used  $k_{31}$  effectively is possible. For  $d_{33}$ , 800 or more pC/N and  $k_{31}$  are [  $k_{33}$  ] coincidence at 30% or less to coincidence in 80% or more.  $-d_{31}$  is 300 pC/N (the definition top  $d_{31}$ ). When it was made the following with a negative value, since there was no spurious (unnecessary vibration) generating into the use band, the value of  $k_{33}$  could be used still more efficiently, and it discovered that the piezo-electric single crystal component of lengthwise direction oscillation mode ( $k_{33}$ ) use of high performance was obtained more.

[0004] Furthermore, the electromechanical coupling coefficient ( $k_{31}$ ) of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization while it has a big electromechanical coupling coefficient ( $k_{33}$ ) in the direction of polarization (lengthwise direction oscillation mode) is small. The domain structure formed of the electric dipole about the direction of polarization of a piezo-electric single crystal component where polarization of the cause

of having dispersion was carried out, and the direction which intersects perpendicularly is not a single domain. It found out that the piezo-electric single crystal component of the following (A) and (B) was obtained that it is because it is formed in two or more domains (multi-domain), and by controlling this domain structure.

[0005] (A) In the piezo-electric single crystal ingredient which is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$  electromechanical coupling coefficient  $k_{31} \geq 70\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization -- and It has piezo-electric distorted constant- $d_{31} \geq 1200 \text{ pC/N}$ . And the domain control piezo-electricity single crystal component which is value  $f_{c31} \leq 650 \text{ Hz}\cdot\text{m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=\text{fr}\cdot L$ ) which is the product of the oscillating lay length (L) of a component.

[0006] (B) In the piezo-electric single crystal ingredient which is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$  electromechanical coupling coefficient  $k_{31} \leq 30\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization -- and It has piezo-electric distorted constant- $d_{31} \leq 300 \text{ pC/N}$ . And the domain control piezo-electricity single crystal component which is value  $f_{c31} \geq 800 \text{ Hz}\cdot\text{m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=\text{fr}\cdot L$ ) which is the product of the oscillating lay length (L) of a component.

[0007] Moreover, it discovered that the conditions which control domain structure were arranged with the value of the frequency constant ( $f_{c31}=\text{fr}\cdot L$ ) which is the resonance frequency (fr) of the oscillation mode and the product of the oscillating lay length (L) of a component in connection with the electromechanical coupling coefficient  $k_{31}$  of the direction of polarization of this piezo-electric single crystal component, and the direction (longitudinal direction oscillation mode) which intersects perpendicularly.

[0008] This invention aims at offering such a piezo-electric single crystal component by which domain control was carried out, and its manufacture approach.

[0009]

[Means for Solving the Problem] In the piezo-electric single crystal ingredient which invention of the 1st of this invention is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$  It is electromechanical coupling coefficient  $k_{31} \geq 70\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization, and is piezo-electric distorted constant- $d_{31} \geq 1200 \text{ pC/N}$  (the definition top d31). It has. a negative value -- having -- And it is the domain control piezo-electricity single crystal component characterized by being value  $f_{c31} \leq 650 \text{ Hz}\cdot\text{m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=\text{fr}\cdot L$ ) which is the product of the oscillating lay length (L) of a component.

[0010] Next, invention of the 2nd of this invention is set into the piezo-electric single crystal ingredient which is electromechanical coupling coefficient  $k_{33} \geq 80\%$  of the lengthwise direction oscillation mode of the direction of polarization, and has piezo-electric distorted constant  $d_{33} \geq 800 \text{ pC/N}$ . It is electromechanical coupling coefficient  $k_{31} \leq 30\%$  of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization, and is piezo-electric distorted constant- $d_{31} \leq 300 \text{ pC/N}$  (the definition top d31). It has. a negative value -- having -- And it is the domain control piezo-electricity single crystal component characterized by being value  $f_{c31} \geq 800 \text{ Hz}\cdot\text{m}$  of the resonance frequency (fr) of the longitudinal direction oscillation mode of the direction which intersects perpendicularly in the direction of polarization about  $k_{31}$ , and the frequency constant ( $f_{c31}=\text{fr}\cdot L$ ) which is the product of the oscillating lay length (L) of a component.

[0011] A slenderness ratio makes the longitudinal direction the direction of polarization about three

or more rod-like structures, and the piezo-electric single crystal component expresses vibration (lengthwise direction vibration) of the direction of polarization when applying an electrical potential difference in the direction of polarization, and the conversion efficiency of distorted magnitude with the electromechanical coupling coefficient ( $k_{33}$ ) and the piezo-electric distorted constant ( $d_{33}$ ) of the lengthwise direction oscillation mode, respectively, and it is so efficient that these numeric values are large. It is specified also about the thing of the configuration of a rectangular plate besides a rod-like structure, a disk, etc. This invention is the domain control piezo electric crystal single crystal component which paid its attention to the electromechanical coupling coefficient ( $k_{31}$ ) of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization.

[0012] As a piezo-electric single crystal ingredient concerning the 1st above-mentioned invention or the 2nd invention, following (a) or (b) can be used suitably.

[0013] (a) It is the solid solution which consists of  $X\text{-Pb(A1, A2, --, B1, B-2--)} \text{O}_3 + (1-X) \text{PbTiO}_3$  ( $0 < X < 1$ ). 1 or two or more elements which were chosen from the group which A1, A2, and -- become from Zn, Mg, nickel, Lu, In, and Sc, B1, and B-2-- are the elements of the 1 and the number of simplicity and complexity which were chosen from the group which consists of Nb, Ta, Mo, and W. The percentage in a1, a2 --, and a chemical formula for the ionic valency of A1, A2, and --, respectively Y1, Y2 --, B1, B-2 -- The percentage in b1, b2 --, and a chemical formula for ionic valency, respectively Z1, Z2 --, The total W of the ionic valency of the element group [ in / when it carries out / chemical formula  $\text{Pb(A1Y1a1, A2Y2a2, --, B1Z1b1, and B2Z2b2--)} \text{O}_3$  ] in a parenthesis is  $W=a_1\text{and}Y_1+a_2Y_2+ \dots b_1\text{and}Z_1+b_2Z_2+ \dots$  Fill the charge of =4+.

[0014] (b) Do 0.5 ppm-1 mass % addition of 1 of Mn and Cr\*\*, or two sorts at the above (a).

[0015] In addition, there is a piezo electric crystal single crystal ingredient (PZN-PT or PZNT, and the latter are called PMN-PT or PMNT for the former) which consists of the solid solution of lead-zinc-niobate  $\text{Pb}(\text{Zn1/3Nb 2/3}) \text{O}_3$ , magnesium lead niobate  $\text{Pb}(\text{Mg1/3Nb 2/3}) \text{O}_3$ , and lead titanate  $\text{PbTiO}_3$  as an ingredient known best.

[0016] There is the manufacture approach shown below as an approach of manufacturing the above domain control piezo-electricity single crystal component.

[0017] One of them is the process (electric-field cooling) cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field as polarization conditions for the thickness direction of a piezo-electric single crystal component, and it is the manufacture approach of the piezo-electric single crystal component characterized by manufacturing the above-mentioned domain control piezo-electricity single crystal component.

[0018] Although this manufacture approach is a process which performs final polarization of a domain control single crystal piezoelectric device, its manufacture approach of adding the process which impresses electric field in the direction of polarization and the direction which intersects perpendicularly, and controls the alignment condition of the ferroelectric domain of the direction of polarization and the direction which intersects perpendicularly to the preceding paragraph of this process is also effective. As a class of electric field impressed in the direction of polarization, and the direction which intersects perpendicularly, there are attenuation electric field besides direct-current electric field, pulse electric field, alternating current electric fields, and these stationary electric fields etc., and field strength, impression time amount, temperature conditions, etc. have proper conditions according to the value of a request of the electromechanical coupling coefficient ( $k_{31}$ ) of the direction which intersects perpendicularly in each property and direction of polarization of a piezo-electric single crystal component. These can be defined by experiment etc. Moreover, as the aforementioned pulse electric field, unipolars, such as an others and alternating current triangular wave, and a bipolar pulse can be used. [ wave / right-angle ]

[0019] Moreover, the manufacture approach characterized by heating and cooling a single crystal piezoelectric device is in the preceding paragraph of the process which performs final polarization of the domain control single crystal piezoelectric device cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 above-mentioned degrees C temperature requirement for a maximum of 2 hours, or impressing electric field as an option of this invention. For example, the temperature field where a piezo-electric single crystal component serves as

rhombohedral, \*\*\*\*\* , and a cubic was decided according to the presentation. Therefore, for example, the process which carries out heating cooling of the single crystal piezoelectric device on both sides of the transition temperature of rhombohedral [ which is the hypothermic phase of this piezo-electric single crystal ingredient ], and \*\*\*\*\* which is a moderate temperature phase (1), Or Curie temperature which is \*\*\*\*\* of this piezo-electric single crystal ingredient, a ferroelectricity, and piezoelectric disappearance temperature (at an elevated temperature, from this temperature) this \*\*\*\*\* single crystal ingredient -- a cubic (parent phase) -- becoming -- the process (2) which inserts and carries out heating cooling -- Or the process which carries out heating cooling within a parent phase (3), Or the process (4) which combines a process (1), (2), and (3) suitably is performed.

Subsequently, by performing the process cooled impressing 400v/mm - 1500v [/mm ] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field, the alignment condition of the ferroelectric domain of the direction which intersects perpendicularly in the direction of polarization is controllable.

[0020] In furthermore, the preceding paragraph of the process which performs final polarization of the process domain control single crystal piezoelectric device cooled impressing 400v/mm - 1500v [/mm ] direct-current electric field in a 20 degrees C - 200 above-mentioned degrees C temperature requirement for a maximum of 2 hours, or impressing electric field The process which impresses electric field in the direction which intersects perpendicularly in the direction of polarization of a single crystal piezoelectric device, By performing the process which uses together the process which carries out heating cooling of the single crystal piezoelectric device, and performing the process cooled impressing 400v/mm - 1500v [/mm ] direct-current electric field subsequently in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field The ferroelectric domain alignment condition of the direction which intersects perpendicularly in the direction of polarization is controllable.

[0021]

[Embodiment of the Invention] For example, the solid-solution single crystal of zinc niobic acid-lead titanate (PZN-PT or PZNT) is making the perovskite structure (ABO<sub>3</sub>) as the unit lattice showed typically to drawing 1 . The phase diagram by the presentation ratio of PZN and PT was shown in drawing 2 . This drawing is Nomura. et al., J.Phys. (1969). J. Kuwata et It quotes from at. and Ferroelectrics (1981). In rhombohedral [ PZNT ], it has the spontaneous polarization which corresponds in the eight directions of <111> bearings of the crystal when regarding as a pseudo-cubic at an electric dipole so that drawing 2 may see. If electric field are impressed to such a spontaneous polarization condition in the \*\*\* <100> direction (the crystal logging direction), an electric dipole will rotate in the polarization electric-field impression direction, and the direction of spontaneous polarization will come to gather.

[0022] However, although various conditions arise in this way of gathering by the mode of impression of electric field etc., consequently the electromechanical coupling coefficient (k33) of the direction of polarization has 80% or more of value in it It turned out that the electromechanical coupling coefficient (k31) of the direction which intersects perpendicularly in the direction of polarization is distributed to 49 - 62% with dispersion according to the reference etc., i.e., control of an electromechanical coupling coefficient (k31) is not made about the direction of polarization, and the direction (transverse-oscillation mode) which intersects perpendicularly. In such a value of k31, it was difficult to produce the device which used k31 positively, or spurious one occurred in the lengthwise direction oscillating (k33) mode of the direction of polarization in the device which uses k33 positively on the other hand, and the situation that sufficient property could not be acquired had occurred. The factor which gives this result is explained as follows. That is, for the material of the piezo-electric single crystal component started from the piezo electric crystal single crystal after training, the domain which consists of a set of the electric dipole of the same direction in the direction of polarization and the direction of polarization, and the direction that intersects perpendicularly has turned to various directions, and does not show piezoelectric, but is in the condition of non-polarization.

[0023] General polarization processing temperature and applied voltage can be chosen, and many domains will not be able to gather without impressing electric field in the direction of polarization in the direction of polarization. By this, the electromechanical coupling coefficient k33 of the direction

of polarization comes to show 80% or more of big value. However, the condition of the domain in the direction of polarization and the direction which intersects perpendicularly can be controlled only within limits with suitable the polarization conditions in the direction of polarization, i.e., polarization processing temperature, and applied voltage.

[0024] Next, an example is given and explained about how to control the mode of polarization. Table 1 shows the dielectricity and the piezo-electric property at the time of changing the polarization conditions of the piezo-electric single crystal ingredient in connection with the conventional example (sample numbers 1, 2, and 3), a reference value (reference values 1 and 2), and this invention etc. d33 value in Table 1 was measured by d33 m (Chinese Academy of Sciences \*\*\*\* lab ZJ-3D mold). It asked for calculation of k33 value from d33vsk33 curve based on this invention persons' measurement shown in drawing 12. k31, d31, and fc31 measured the frequency response of an impedance, and computed it by count. The piezo-electric single crystal component (component configuration: 13mm die-length x4mm width-of-face x0.36mm thickness) of used 0.91PZN(s) +0.09PT (it expresses with X= 0.91 and a mole fraction) As shown in drawing 3, the 6th page produces a golden electrode by the spatter to two fields (001) 11 of the crystal 10 surrounded in the field (100) which counter, and it is immersed into a 40-degree C silicone oil. To inter-electrode, 250v [ mm ] (sample number 4) /and 500v (sample number 5)/mm After impressing each [ 700v / mm / (sample number 6) /, 1000v / mm / (sample number 7) /, and 1600v //mm / (sample number 8) ] electric field for 10 minutes, the impedance curve in the k31 mode was shown in drawing 4 - drawing 8. It is in the condition that mm is [v / ( drawing 4 ) // 250 ] inadequate in polarization, and although three k31 oscillation modes are seen by mm in 500v [ mm ] ( drawing 5 ) /and 700v ( drawing 6 ) /, this is because there are two or more domains in the direction which intersects perpendicularly in the direction of polarization.

[0025] The domain in the direction which intersects perpendicularly in the direction of polarization is a single domain, and as for the value of k31, k33 of the direction of polarization shows >95% at the same time it fills >80%, so that clearly [v / ( drawing 7 ) //mm / 1000 ] from an impedance curve. Although it separated into two or more domains again in mm in 1600v ( drawing 8 ) /and the value of k33 was >95%, the value of k31 is 61%. Moreover, the values fc31 of the frequency constant (fc31=fr-L) which is the resonance frequency (fr) of the longitudinal direction oscillation mode and the product of the oscillating lay length (L) of a component about k31 of each sample were [ in the sample number 4 / in 741 Hz-m and a sample number 5 / in 601 Hz-m and a sample number 6 ] 700 Hz-m in 522 Hz-m and a sample number 8 at 603 Hz-m and a sample number 7. The condition of the domain within the field which intersects perpendicularly in the direction of polarization after 250v /, 500v /, 1000v /, and 1600v [/mm ] impression mm mm is shown in drawing 9 . [ mm ]

[0026] In drawing 9 , although mm is [v // 250 ] inadequate in polarization and it is two or more domains (multi-domain) in mm in 500v /, k31 becomes large by the synergism of the polarization component in connection with k31. By mm, it becomes a single domain in 1000v /, and by mm, it becomes two or more domains in 1600 morev /, and k31 becomes small by the phase bactericidal action of the polarization component in connection with k31. the inside of this invention -- high -- k33 (d33) -- high -- the domain arrays from which k31 (d31) is obtained were 500v [ mm ] /and 1000v/mm. When the temperature of a silicone oil was dropped to the room temperature, impressing 400v [/mm ] direct-current electric field for the component of the same setup, and a sample number 9 in a 200-degree C silicone oil on the other hand, the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) was >=80%, and the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization was >70%. fc31 at this time was 609 Hz-m. In the sample number 10, the component of the same setup was immersed into the 60-degree C silicone oil, and 400v [/mm ] direct-current electric field were impressed for 120 minutes. Consequently, although the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) was >95%, the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization was <30%.

[0027] Moreover, although the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) was >90% in the sample number 11 when 1500v

[/mm] direct-current electric field were impressed to the component of the same setup for 10 minutes, the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization was <30%. fc(s)31 of a sample number 10 and a sample number 11 were 981 Hz-m and 1004 Hz-m, respectively. It is thought that this result comes from the domain array which suppresses longitudinal direction vibration.

[0028] Thus, by setting up polarization conditions (applied voltage, temperature, etc.) appropriately, the domain condition at the time of polarization and the value of k33 and k31 depending on it are controllable. moreover, the thing for which the temperature requirement, the polarization electric-field value range, impression time amount range, and the impression approach of the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field not only in the example shown here but in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field are used -- the above-mentioned example of \*\*\*\* -- \*\* -- it is checked that same dielectricity and piezo-electric property are acquired.

[0029] Furthermore, it is related with the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field. The process of the depolarization held at 200 degrees C more than Curie temperature for 1 hour is inserted. It is checked also by repeating the process of the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field that the property shown in the 1st invention and the 2nd invention improves. These results The direction which intersects perpendicularly in the direction of polarization as [ show / in drawing 10 / when it arranges with the value of the electromechanical coupling coefficient k31 of the (longitudinal direction oscillation mode), the resonance frequency (fr) in the k31 mode, and the frequency constant (fc31=fr-L) that is the product of the oscillating lay length (L) of a component ] -- high -- k33 -- high -- the field of k31 -- high -- k33 -- It turned out that a field low [ k31 ] is obtained considering the range of the value of a frequency constant (fc31=fr-L) as an axis of abscissa.

[0030] Although the conventional example and the reference value were also indicated to coincidence at drawing 10 In the conventional example and a reference value, there is a value of the resonance frequency (fr) in the k31 mode and the frequency constant (fc31=fr-L) which is the product of the oscillating lay length (L) of a component in the middle of claims 1 and 2 of this invention. As clarified by this invention, it is in the field where the domain control of the direction of polarization and the direction which intersects perpendicularly is inadequate, therefore it is thought that the value of k31 varies.

[0031] Next, the process which controls the direction of the ferroelectric domain of the direction which impresses electric field in the direction which intersects perpendicularly in the direction of polarization of a single crystal piezoelectric device, and intersects perpendicularly in the direction of polarization, The process which carries out heating cooling of the single crystal piezoelectric device on both sides of the transition temperature of rhombohedral [ which is the hypothermic phase of this piezo-electric single crystal ingredient ], and \*\*\*\*\* which is a moderate temperature phase (1), Or the process which carries out heating cooling on both sides of the Curie temperature which is \*\*\*\*\* of this piezo-electric single crystal ingredient, a ferroelectricity, and piezoelectric disappearance temperature (2), Or the process which carries out heating cooling within a parent phase (3), Or the process (4) which combined suitably said process (1), (2), and (3) is performed. Subsequently, the example which performed the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field is \*\*(ed) and explained in Table 2. The measurement of d33 in Table 2, calculation of k33 value, measurement of k31, d31, and fc31, and count are the same as that of Table 1.

[0032] Before the process of the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field in a sample number 12 The golden electrode was produced by the spatter to two fields (010) 13 which intersect perpendicularly with the field (001) 11 of drawing 3 , and counter the component of the same configuration as the above-mentioned single crystal piezo

electric crystal component as shown in drawing 11, and in the 40-degree C silicone oil, 1000v [/mm] direct-current electric field were impressed for 10 minutes, and were polarized. The process cooled the etching reagent's having removed this golden electrode, producing a golden electrode by the spatter to two fields (001) 11 which is further shown in drawing 3, and which counter, and impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in the above-mentioned example for a maximum of 2 hours, or impressing electric field after taking out a component was carried out, and dielectricity and a piezo-electric property were measured.

[0033] Consequently, as shown in the sample number 12 of Table 2, 2810 pC/N was obtained by the piezo-electric distorted constant d33 97.3% with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode). Moreover, -2380 pC/N was obtained by the piezo-electric distorted constant d31 85.5% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of the frequency constant (fc31=fr-L) which is the resonance frequency (fr) of the longitudinal direction oscillation mode and the product of the oscillating lay length (L) of a component about k31 was 483 Hz-m.

[0034] Before the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field in sample numbers 13, 14, and 15 The component of the same configuration as the above-mentioned single crystal piezo electric crystal component was immersed into the silicone oil, respectively, and a 3 times temperature rise and descent were further repeated [ the temperature requirement (50-90 degrees C and 150-200 degrees C) ] for the 200-400-degree C temperature requirement in a cycle of 30 minutes within the temperature tub. Then, the golden electrode was produced by the spatter to two fields (001) 11 which is shown in drawing 3 and which counter, the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in the above-mentioned example for a maximum of 2 hours, or impressing electric field was carried out, and dielectricity and a piezo-electric property were measured. Consequently, at the sample number 13, 2840 pC/N was obtained by the piezo-electric distorted constant d33 97.5% with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode).

[0035] Moreover, it was the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization, and 85.3%, by the piezo-electric distorted constant d31, -2360 pC/N was obtained with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode), and 2880 pC/N was obtained by the piezo-electric distorted constant d33 97.8% at the sample number 14.

[0036] Moreover, it was the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization, and 85.3%, by the piezo-electric distorted constant d31, -2350 pC/N was obtained with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode), and 2820 pC/N was obtained by the piezo-electric distorted constant d33 97.4% at the sample number 15. Moreover, -2380 pC/N was obtained by the piezo-electric distorted constant d31 85.6%, respectively with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of a frequency constant (fc31=fr-L) was [ at 503 Hz-m and a sample number 14 ] 437 Hz-mm in the sample number 13 in 506 Hz-m and a sample number 15.

[0037] In the sample number 16, 400v [/mm] direct-current electric field were impressed, having produced the golden electrode by the spatter to two fields (010) 13 which intersect perpendicularly with the field (001) 11 of drawing 3, and counter, as shown in drawing 11, having been immersed into the silicone oil, and repeating a 3 times temperature rise and descent for a 150-200-degree C temperature requirement in a cycle of 30 minutes. The process cooled the etching reagent's having removed this golden electrode, producing a golden electrode by the spatter to two fields (001) 11 which is further shown in drawing 3, and which counter, and impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in

the above-mentioned example for a maximum of 2 hours, or impressing electric field after taking out a component was carried out, and dielectricity and a piezo-electric property were measured. Consequently, 2870 pC/N was obtained by the piezo-electric distorted constant d33 97.8% with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode). Moreover, -2450 pC/N was obtained by the piezo-electric distorted constant d31 86.0% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of a frequency constant (fc31=fr-L) was 415 Hz-m.

[0038] In addition, it intersects perpendicularly with the field (001) of drawing 3, and as another field which counters, after impressing direct-current electric field to face-to-face [ of drawing 11 ] (100), even if it carries out the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field, it is checking that the same effectiveness is acquired.

[0039] Before the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field in a sample number 17 A golden electrode is attached to two fields (010) 13 which intersect perpendicularly with the field (001) 11 of drawing 3, and counter the component of the same configuration as the above-mentioned single crystal piezo electric crystal component as shown in drawing 11 by the spatter. The peak value of 500v/mm and the bipolar triangular wave electric field of periodic 800msec were impressed for 10 minutes in the 60-degree C silicone oil. The wave of a bipolar triangular wave was shown in drawing 13. The process cooled the etching reagent's having removed this golden electrode, producing a golden electrode by the spatter to two fields (001) 11 which is further shown in drawing 3, and which counter, and impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in the above-mentioned example for a maximum of 2 hours, or impressing electric field after taking out a component was carried out, and dielectricity and a piezo-electric property were measured. Consequently, 2780 pC/N was obtained by the piezo-electric distorted constant d33 97.1% with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode). Moreover, -230 pC/N was obtained by the piezo-electric distorted constant d31 18.3% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of a frequency constant (fc31=fr-L) was 863 Hz-m.

[0040] Before the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field in sample numbers 18, 19, and 20 The component of the same configuration as the above-mentioned single crystal piezo electric crystal component was immersed into the silicone oil, respectively, and a 3 times temperature rise and descent were repeated for the temperature requirement (50-90 degrees C, 150-200 degrees C, and 200-400 degrees C) in a cycle of 5 minutes. Then, the golden electrode was produced by the spatter to two fields (001) 11 which is shown in drawing 3 and which counter, the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in the above-mentioned example for a maximum of 2 hours, or impressing electric field was carried out, and dielectricity and a piezo-electric property were measured.

[0041] consequently -- a sample number 18 -- the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) -- 97.0% and the piezo-electric distorted constant d33 -- 2760 pC/N -- moreover, -260 pC/N was obtained by the piezo-electric distorted constant d31 18.6% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. a sample number 19 -- the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) -- 97.3% and the piezo-electric distorted constant d33 -- 2810 pC/N -- moreover, -190 pC/N was obtained by the piezo-electric distorted constant d31 17.8% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization.

[0042] a sample number 20 -- the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode) -- 97.2% and the piezo-electric distorted constant d33 -- 2790 pC/N -- moreover, -220 pC/N was obtained by the piezo-electric distorted constant d31 18.2%, respectively with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of a frequency constant (fc31=fr-L) was [ at 836 Hz-m and a sample number 19 ] 847 Hz-m in the sample number 18 in 892 Hz-m and a sample number 20.

[0043] In the sample number 21, 400v [/mm] direct-current electric field were impressed, having produced the golden electrode by the spatter to two fields (010) 13 which intersect perpendicularly with the field (001) 11 of drawing 3, and counter, as shown in drawing 11, having been immersed into the silicone oil, and repeating a 3 times temperature rise and descent for a 150-200-degree C temperature requirement in a cycle of 5 minutes. The process cooled the etching reagent's having removed this golden electrode, producing a golden electrode by the spatter to two fields (001) 11 which is further shown in drawing 3, and which counter, and impressing 400v/mm - 1500v [/mm] direct-current electric field in the 20 degrees C - 200 degrees C temperature requirement shown in the above-mentioned example for a maximum of 2 hours, or impressing electric field after taking out a component was carried out, and dielectricity and a piezo-electric property were measured.

Consequently, 2850 pC/N was obtained by the piezo-electric distorted constant d33 97.7% with the electromechanical coupling coefficient k33 of the direction of polarization (lengthwise direction oscillation mode). Moreover, -150 pC/N was obtained by the piezo-electric distorted constant d31 17.6% with the electromechanical coupling coefficient k31 of the direction (longitudinal direction oscillation mode) which intersects perpendicularly in the direction of polarization. The value fc31 of a frequency constant (fc31=fr-L) was 924 Hz-m.

[0044] The process which performs final polarization on the occasion of the above-mentioned domain control piezo-electricity single crystal component, In namely, the preceding paragraph of the process cooled impressing 400v/mm - 1500v [/mm] direct-current electric field in a 20 degrees C - 200 degrees C temperature requirement for a maximum of 2 hours, or impressing electric field How to impress electric field in the direction of polarization, and the direction which intersects perpendicularly, and control the alignment condition of the ferroelectric domain of the direction of polarization, and the direction which intersects perpendicularly, The process which carries out heating cooling on both sides of the transition temperature of rhombohedral [ which is the hypothermic phase of a piezo-electric single crystal ingredient ], and \*\*\*\*\* which is a moderate temperature phase (1), Or Curie temperature which is \*\*\*\*\* of a piezo-electric single crystal ingredient, a ferroelectricity, and piezoelectric disappearance temperature (at an elevated temperature, from this temperature) this piezo electric crystal single crystal ingredient -- a cubic (parent phase) -- becoming -- the process (2) which inserts and carries out heating cooling -- Or the process which carries out heating cooling within a parent phase (3), Or the approach of controlling the alignment condition of the ferroelectric domain of the direction which intersects perpendicularly with the direction of polarization according to the process (4) which combined a process (1), (2), and (3) suitably and the process which impresses electric field in the direction which intersects perpendicularly in the direction of polarization of a single crystal piezoelectric device, Enforcing the approach of controlling the alignment condition of the ferroelectric domain of the direction which intersects perpendicularly with the direction of polarization according to the process which uses together the process which carries out heating cooling of the single crystal piezoelectric device Two or more domains under crystal generated in the annealing process at the time of crystal training by carrying out each above-mentioned process The domain structure of the direction which intersects perpendicularly in the direction of polarization in the process which performs final polarization of the domain control single crystal piezoelectric device which should be controlled more nearly human and manufactures the above-mentioned domain control piezo-electricity single crystal component In order to raise the dielectricity and the piezo-electric property as used in the field of effective in order to control more easily and invention of the 1st of this invention, and the 2nd invention, it turned out that it is effective.

[0045]

[Effect of the Invention] The domain control piezo electric crystal single crystal component and its

manufacture approach of this invention Since it is constituted as mentioned above, for d<sub>33</sub>, 800 or more pC/N and \*\*\*\* k<sub>31</sub> are [ k<sub>33</sub> ] coincidence at 70% or more to coincidence in 80% or more. - d<sub>31</sub> is 1200 pC/N (the definition top d<sub>31</sub>). More than it had a negative value, when it carries out, manufacture of the piezo-electric single crystal component which used k<sub>31</sub> effectively is possible. For d<sub>33</sub>, 800 or more pC/N and k<sub>31</sub> are [ k<sub>33</sub> ] coincidence at 30% or less to coincidence in 80% or more. - d<sub>31</sub> is 300 pC/N (the definition top d<sub>31</sub>). When it was made the following with a negative value, since there was no spurious generating into the use band of the oscillation mode of k<sub>33</sub>, the k<sub>33</sub> mode could be used still more efficiently, and it became possible to obtain the piezo-electric single crystal component of lengthwise direction (k<sub>33</sub>) oscillation mode use of high performance more.

[0046]

[Table 1]

試料番号	分極条件			誘電・圧電特性					適用される 請求項等
	温度 ℃	電界 E V/mm	時間 min	k <sub>33</sub> %	d <sub>33</sub> 10 <sup>-12</sup> C/N	k <sub>31</sub> %	d <sub>31</sub> 10 <sup>-12</sup> C/N	f <sub>C<sub>31</sub></sub> Hz · m	
1	20	1800	10	95.6	2550	61.5	-970	701	従来例
2	60	400	150	95.3	2500	48.7	-694	773	従来例
3	100	300	120	94.0	2360	35.0	-520	755	従来例
4	40	250	10	56.0	165	18.9	-224	741	分極不十分
5	40	500	10	84.0	1190	76.0	-1310	601	請求項 1
6	40	700	10	87.0	1420	77.1	-1324	603	請求項 1
7	40	1000	10	95.3	2500	80.8	-1701	522	請求項 1
8	40	1600	10	95.3	2500	60.9	-939	700	請求項 1
9	200	400	電界冷却	80.2	960	74.7	-1263	609	請求項 1
10	60	400	120	96.9	2740	26.3	-288	981	請求項 2
11	20	1500	10	94.6	2300	27.1	-291	1004	請求項 2
文献値 1				94	2300	53	-1100	-	
文献値 2				90	1734	49	-962	680.733 (平均値 : 707)	

[0047]

[Table 2]

試料番号	処理内容	条件	誘電・圧電特性					対応する 請求項
			k <sub>33</sub> %	d <sub>33</sub> 10 <sup>-12</sup> C/N	k <sub>31</sub> %	d <sub>31</sub> 10 <sup>-12</sup> C/N	f <sub>C<sub>31</sub></sub> Hz · m	
12	請求項 5	直流電界 1000V/mm、40℃、10 分	97.3	2810	85.5	-2380	483	請求項 1
13	請求項 6	50~90℃、30 分周期、繰り返し 3 回	97.5	2840	85.3	-2360	503	請求項 1
14	請求項 6	150~200℃、30 分周期、繰り返し 3 回	97.8	2880	85.3	-2350	506	請求項 1
15	請求項 6	200~400℃、80 分周期、繰り返し 3 回	97.4	2820	85.6	-2380	437	請求項 1
16	請求項 7	直流電界 400V/mm、150~200℃、30 分周期、繰り返し 3 回	97.8	2870	86.0	-2450	415	請求項 1
17	請求項 5	バイポーラ三角波 500V/mm、周期 800ms、10 分	97.1	2780	18.3	-230	863	請求項 2
18	請求項 6	50~90℃、5 分周期、繰り返し 3 回	97.0	2760	18.6	-260	836	請求項 2
19	請求項 6	150~200℃、5 分周期、繰り返し 3 回	97.3	2810	17.8	-190	892	請求項 2
20	請求項 6	200~400℃、5 分周期、繰り返し 3 回	97.2	2790	18.2	-220	847	請求項 2
21	請求項 7	直流電界 400V/mm、150~200℃、5 分周期、繰り返し 3 回	97.7	2850	17.6	-150	924	請求項 2

[Translation done.]

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3. In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

- [Drawing 1] It is the typical perspective view of the crystal structure.  
[Drawing 2] It is the phase diagram of PZN-PT (PZNT). .  
[Drawing 3] It is the explanatory view of electric-field impression.  
[Drawing 4] It is drawing of the impedance curve of k31 oscillation mode.  
[Drawing 5] It is drawing of the impedance curve of k31 oscillation mode.  
[Drawing 6] It is drawing of the impedance curve of k31 oscillation mode.  
[Drawing 7] It is drawing of the impedance curve of k31 oscillation mode.  
[Drawing 8] It is drawing of the impedance curve of k31 oscillation mode.  
[Drawing 9] It is drawing of the condition of the domain within the direction (thickness direction) side of polarization after electric-field impression.  
[Drawing 10] It is the graph of the value of an electromechanical coupling coefficient k31, the resonance frequency (fr) of k31 oscillation mode, and the frequency constant (fc31=fr-L) that is the product of the oscillating lay length (L) of a component.  
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[Drawing 12] It is the graph of k33 pair d33.  
[Drawing 13] It is the wave form chart of a bipolar triangular wave pulse.  
[Description of Notations]  
10 Piezo-electric Single Crystal Component  
11 Electrode Surface (001)  
12 Electric Field  
13 Electrode Surface (010)
- 

[Translation done.]

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10 Piezo-electric Single Crystal Component

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12 Electric Field

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[Translation done.]

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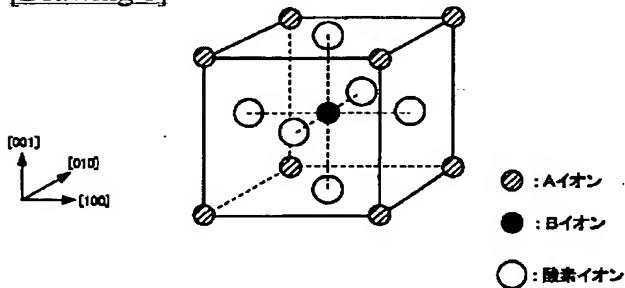
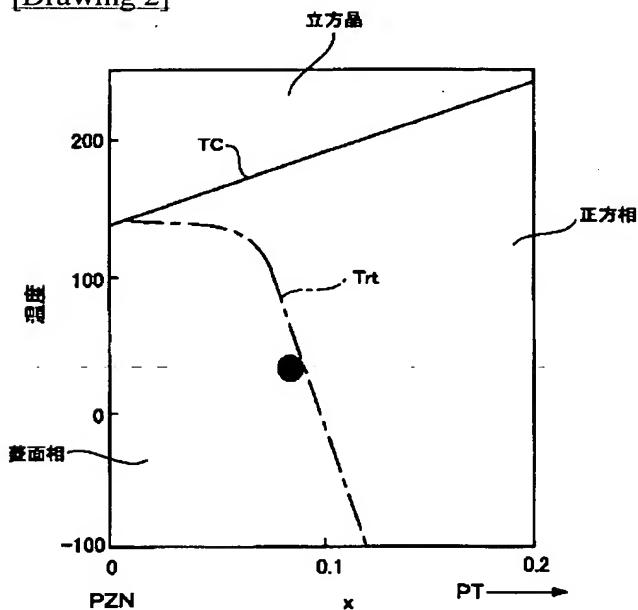
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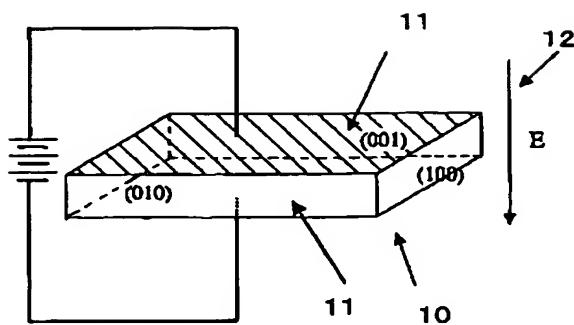
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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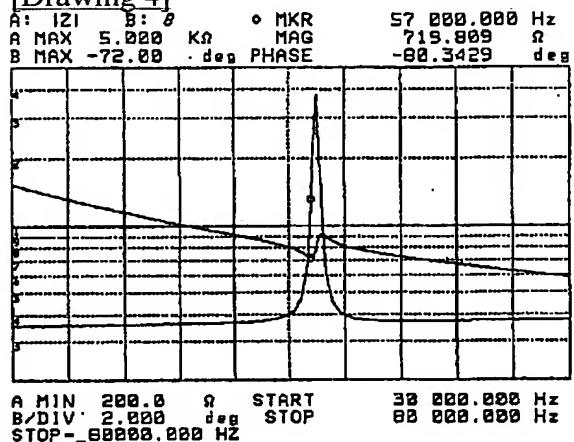
**DRAWINGS**

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**[Drawing 1]****[Drawing 2]****[Drawing 3]**

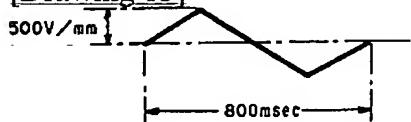


[Drawing 4]

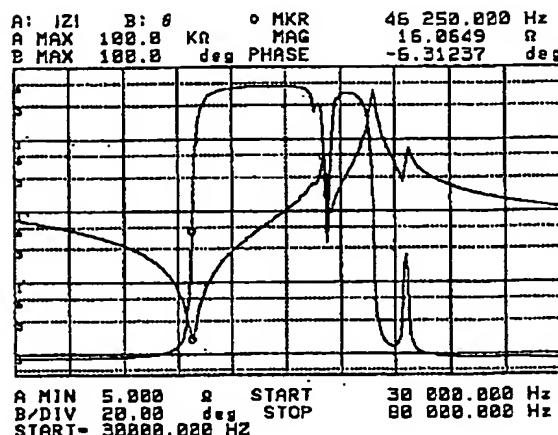


250V/mm

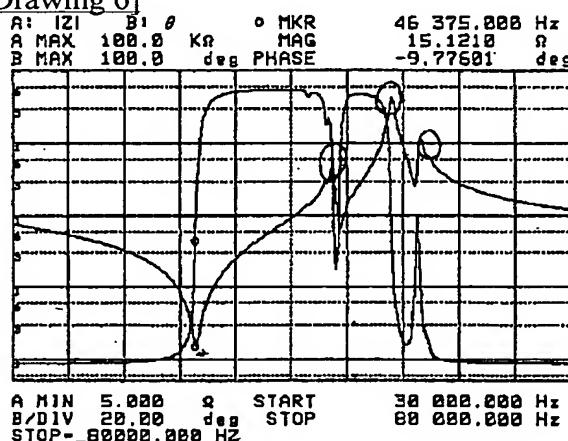
[Drawing 13]



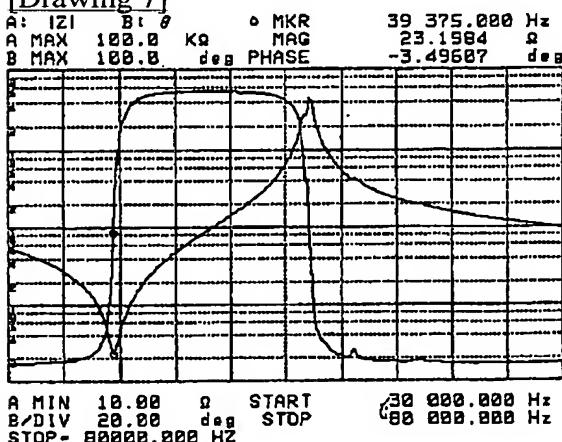
[Drawing 5]



500V/mm

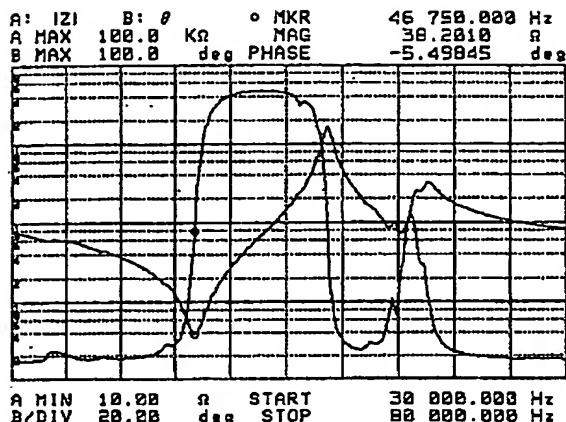
[Drawing 6]

700V/mm

[Drawing 7]

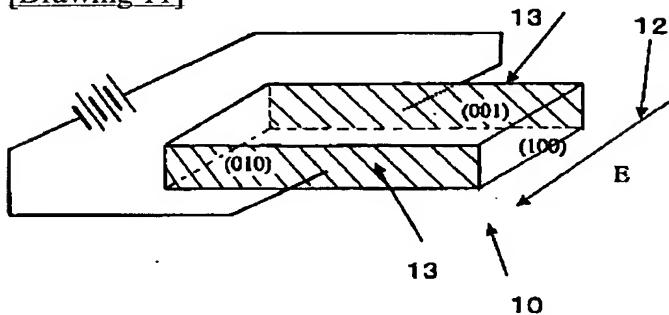
1000V/mm

[Drawing 8]

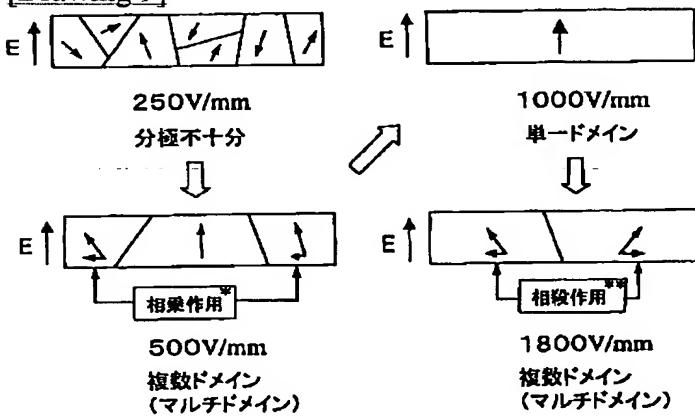


1600 V/mm

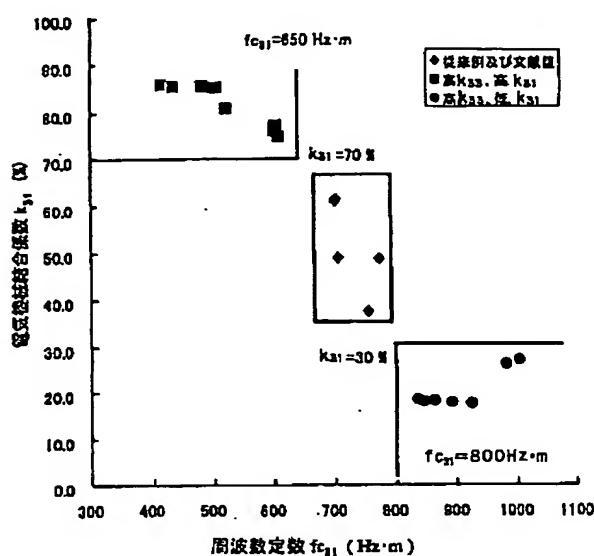
[Drawing 11]



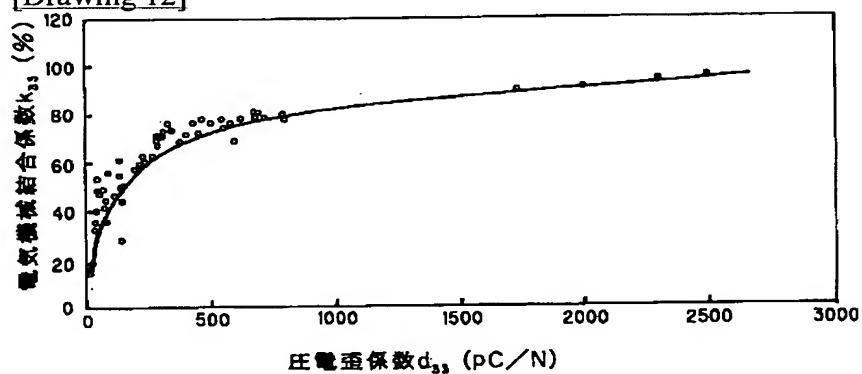
[Drawing 9]

\* 相乗作用で  $k_{31}$  が大きくなる。\*\* 相殺作用で  $k_{31}$  が小さくなる。

[Drawing 10]



[Drawing 12]



[Translation done.]

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研究討論会」において文書をもって発表

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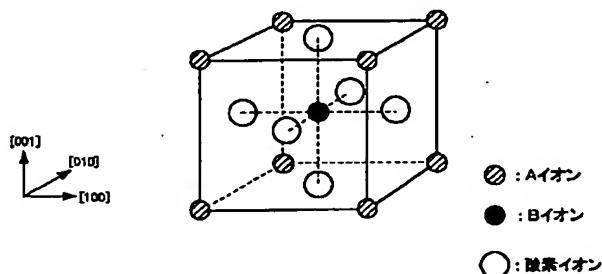
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(54)【発明の名称】 ドメイン制御圧電単結晶素子及びその製造方法

(57)【要約】

【課題】  $k_{33}$ が80%以上で  $d_{33}$ が800 pC/N以上、且つ  $k_{31}$ が70%以上で  $-d_{31}$ が1200 pC/N以上の  $k_{31}$ を有効に利用した横方向振動モード ( $k_{31}$ ) 利用のドメイン制御圧電単結晶素子、及び  $k_{33}$ が80%以上で  $d_{33}$ が800 pC/N以上、且つ  $k_{31}$ が30%以下で  $k_{33}$ 振動モードの使用帯域内にスプリアス等のない、高効率、高性能の縦方向振動モード ( $k_{33}$ ) 利用のドメイン制御圧電単結晶素子を開発した。

【解決手段】 圧電単結晶素子の厚み方向の分極条件として、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか、電界を印加したまま冷却すること(電界冷却)、この工程の前段として分極方向に直交する方向に電界を印加すること(電界印加)、又は圧電単結晶の菱面晶～正方晶相境界温度、又は正方晶～立方晶相境界温度を挟んで昇降温するか、又は立方晶温度域の異なる2温度間で昇降温する(熱処理)こと、又は、これらを併用する。



## 【特許請求の範囲】

【請求項1】 分極方向の縦方向振動モードの電気機械結合係数  $k_{33} \geq 80\%$  で且つ圧電歪定数  $d_{33} \geq 800 \text{ pC/N}$  を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数  $k_{31} \geq 70\%$  で且つ、圧電歪定数  $-d_{31} \geq 1200 \text{ pC/N}$  を持ち、且つ  $k_{31}$  に関する分極方向に直交する方向の横方向振動モードの共振周波数 ( $f_r$ ) と素子の振動方向の長さ ( $L$ ) の積である周波数定数 ( $f_c$ )  $f_{c31} = f_r \cdot L$  の値  $f_{c31} \leq 650 \text{ Hz} \cdot \text{m}$  であることを特徴とするドメイン制御圧電単結晶素子。

【請求項2】 分極方向の縦方向振動モードの電気機械結合係数  $k_{33} \geq 80\%$  で且つ圧電歪定数  $d_{33} \geq 800 \text{ pC/N}$  を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数  $k_{31} \geq 30\%$  で且つ、圧電歪定数  $-d_{31} \leq 300 \text{ pC/N}$  を持ち、且つ  $k_{31}$  に関する分極方向に直交する方向の横方向振動モードの共振周波数 ( $f_r$ ) と素子の振動方向の長さ ( $L$ ) の積である周波数定数 ( $f_c$ )  $f_{c31} = f_r \cdot L$  の値  $f_{c31} \geq 800 \text{ Hz} \cdot \text{m}$  であることを特徴とするドメイン制御圧電単結晶素子。

【請求項3】 圧電単結晶材料が、下記(a)又は(b)であることを特徴とする請求項1又は請求項2記載のドメイン制御圧電体単結晶素子。

(a)  $X \cdot Pb (A_1, A_2, \dots, B_1, B_2 \dots) O_3 + (1-X) PbTiO_3 (0 < X < 1)$  からなる固溶体であって、 $A_1, A_2, \dots$  は  $Zn, Mg, Ni, Lu, In$  及び  $Sc$  からなる群から選ばれた1又は複数の元素、 $B_1, B_2 \dots$  は  $Nb, Ta, Mo$  及び  $W$  からなる群から選ばれた1又は複数の元素で、 $A_1, A_2, \dots$  のイオン価をそれぞれ  $a_1, a_2 \dots$  、化学式中の構成比を  $Y_1, Y_2 \dots, B_1, B_2 \dots$  のイオン価をそれぞれ  $b_1, b_2 \dots$  、化学式中の構成比を  $Z_1, Z_2 \dots$  とした時に、化学式  $Pb (A_1 Y_1^{a_1}, A_2 Y_2^{a_2}, \dots, B_1 Z_1^{b_1}, B_2 Z_2^{b_2}) O_3$  におけるかっこ内の元素群のイオン価の総和  $W$  が  $W = a_1 \cdot Y_1 + a_2 \cdot Y_2 + \dots + b_1 \cdot Z_1 + b_2 \cdot Z_2 + \dots = 4 +$  の電荷を満たすものであること。

(b) 上記(a)に、 $Mn, Cr$  の1又は2種を  $0.5 \text{ ppm} \sim 1 \text{ 質量\%}$  添加したものであること。

【請求項4】 圧電単結晶素子の厚み方向の分極条件として、 $20^\circ\text{C} \sim 200^\circ\text{C}$  の温度範囲で  $400 \text{ V/mm} \sim 1500 \text{ V/mm}$  の直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を行い、ドメイン制御圧電単結晶素子を製造することを特徴とする圧電単結晶素子の製造方法。

【請求項5】 請求項4に記載の工程の前段階として、単結晶圧電素子の分極方向に直交する方向に電界を印加する工程を行い、分極方向に直交する方向の強誘電体ドメインの方向を制御する工程を行い、次いで請求項4に記載する工程を行うことによりドメイン制御圧電体単結

晶素子を製造することを特徴とする請求項4記載の圧電単結晶素子の製造方法。

【請求項6】 請求項4に記載の工程の前段階として、単結晶圧電素子を該圧電単結晶材料の低温相である菱面晶と中温相である正方晶の転移温度を挟んで加熱冷却する工程(1)、又は該圧電単結晶材料の正方晶と強誘電性・圧電性の消失温度であるキュリー温度を挟んで加熱冷却する工程(2)、又は、キュリー温度以上の高温相である立方晶の温度範囲内で加熱冷却する工程(3)、又は、前記工程(1)、(2)、(3)を適宜組み合わせた工程(4)を行い、次いで請求項4に記載する工程を行うことにより、分極方向に直交する方向の強誘電体ドメインの方向を制御し、ドメイン制御圧電体単結晶素子を製造することを特徴とする圧電単結晶素子の製造方法。

【請求項7】 単結晶圧電素子の分極方向に直交する方向に電界を印加する工程と、単結晶圧電素子を該圧電単結晶材料の低温相である菱面晶と中温相である正方晶の転移温度を挟んで加熱冷却する工程(1)、又は該圧電単結晶材料の正方晶と強誘電性・圧電性の消失温度であるキュリー温度を挟んで加熱冷却する工程(2)、又は、キュリー温度以上の高温相である立方晶の温度範囲内で加熱冷却する工程(3)、又は、前記工程(1)、(2)、(3)を適宜組み合わせた工程(4)を併用する工程を行い、次いで  $20^\circ\text{C} \sim 200^\circ\text{C}$  の温度範囲で  $400 \text{ V/mm} \sim 1500 \text{ V/mm}$  の直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を行い、分極方向に直交する方向の強誘電体ドメインの方向を制御し、ドメイン制御圧電体単結晶素子を製造することを特徴とする圧電単結晶素子の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、圧電単結晶素子及びその製造方法に関する。さらに詳しくは、単結晶材料からなる素子であって、分極方向に直交する方向、即ち横方向振動モードの電気機械結合係数と該方向のドメイン制御に着目した素子及びその製造方法に関する。

## 【0002】

【従来の技術】 圧電単結晶素子については、例えば、特開平6-38963号公報には、亜鉛ニオブ酸チタン酸鉛の固溶単結晶からなる圧電体を用いた超音波プローブが開示されている。この技術は、このような圧電体が分極方向の電気機械結合係数 ( $k_{33}$ ) が  $80 \sim 85\%$  と大きく、この単結晶を使用することにより、感度の良いプローブが得られることを示している。従来、圧電単結晶素子はこのように分極方向の電気機械結合係数について研究され、各種の用途も開発されているが、分極方向に直交する方向の特性については、未開拓の技術分野である。

## 【0003】

【発明が解決しようとする課題】本発明者らは、圧電単結晶素子の分極方向（縦方向振動モード）の電気機械結合係数（ $k_{33}$ ）が $\geq 80\%$ の値を持つことにより、多種の用途に供されているにも拘わらず、分極方向に直交する方向（横方向振動モード）の電気機械結合係数（ $k_{31}$ ）が例えば、IEEE Proc. MEDICAL IMAGING 3664 (1999) pp. 239 やその他の文献に示されるように $4.9\% \sim 6.2\%$ と分極方向（縦方向振動モード）の電気機械結合係数（ $k_{33}$ ）に比較して低い値であり、且つ文献によりばらつきのある値を示すことに着目した。そして鋭意研究した結果、 $k_{33}$ が $80\%$ 以上で同時に $d_{33}$ が $800\text{pC/N}$ 以上、且つ $k_{31}$ が $70\%$ 以上で同時に $-d_{31}$ が $1200\text{pC/N}$ （定義上 $d_{31}$ は、負の値を持つ）以上にした場合は、 $k_{31}$ を有効に利用した圧電単結晶素子の製造が可能であり、 $k_{33}$ が $80\%$ 以上で同時に $d_{33}$ が $800\text{pC/N}$ 以上、且つ $k_{31}$ が $30\%$ 以下で同時に $-d_{31}$ が $300\text{pC/N}$ （定義上 $d_{31}$ は、負の値を持つ）以下にした場合には、 $k_{33}$ の値をその使用帯域内にスプリアス（不要振動）等の発生がないため更に効率よく利用でき、より高性能の縦方向振動モード（ $k_{33}$ ）利用の圧電単結晶素子が得られることを発見した。

【0004】更に、分極方向（縦方向振動モード）で大きな電気機械結合係数（ $k_{33}$ ）を有しながら分極方向に直交する方向（横方向振動モード）の電気機械結合係数（ $k_{31}$ ）が小さく、ばらつきを有する原因是、分極された圧電単結晶素子の分極方向と直交する方向に関する電気双極子により形成されるドメイン構造が單一ドメインでなく、複数個のドメイン（マルチドメイン）で形成されているためであること、そして、該ドメイン構造を制御することにより、次の（A）、（B）の圧電単結晶素子が得られることを見出した。

【0005】（A）分極方向の縦方向振動モードの電気機械結合係数 $k_{33} \geq 80\%$ で且つ圧電歪定数 $d_{33} \geq 800\text{pC/N}$ を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数 $k_{31} \geq 70\%$ で且つ、圧電歪定数 $-d_{31} \geq 1200\text{pC/N}$ を持ち、且つ $k_{31}$ に関する分極方向に直交する方向の横方向振動モードの共振周波数（ $f_r$ ）と素子の振動方向の長さ（ $L$ ）の積である周波数定数（ $f_c = f_r \cdot L$ ）の値 $f_c \leq 650\text{Hz} \cdot m$ であるドメイン制御圧電単結晶素子。

【0006】（B）分極方向の縦方向振動モードの電気機械結合係数 $k_{33} \geq 80\%$ で且つ圧電歪定数 $d_{33} \geq 800\text{pC/N}$ を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数 $k_{31} \leq 30\%$ で且つ、圧電歪定数 $-d_{31} \leq 300\text{pC/N}$ を持ち、且つ $k_{31}$ に関する分極方向に直交する方向の横方向振動モードの共振周波数（ $f_r$ ）と素子の振動方向の長さ（ $L$ ）の積である周波数定数（ $f_c = f_r \cdot L$ ）の値 $f_c \leq 650\text{Hz} \cdot m$ であるドメイン制御圧電単結晶素子。

$L$ ）の値 $f_c \geq 800\text{Hz} \cdot m$ であるドメイン制御圧電単結晶素子。

【0007】また、ドメイン構造を制御する条件が該圧電単結晶素子の分極方向と直交する方向（横方向振動モード）の電気機械結合係数 $k_{31}$ に関する振動モードの共振周波数（ $f_r$ ）と素子の振動方向の長さ（ $L$ ）の積である周波数定数（ $f_c = f_r \cdot L$ ）の値により整理されることを発見した。

【0008】本発明は、このようなドメイン制御された圧電単結晶素子及びその製造方法を提供することを目的とする。

【0009】

【課題を解決するための手段】本発明の第1の発明は、分極方向の縦方向振動モードの電気機械結合係数 $k_{33} \geq 80\%$ で且つ圧電歪定数 $d_{33} \geq 800\text{pC/N}$ を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数 $k_{31} \geq 70\%$ で且つ、圧電歪定数 $-d_{31} \geq 1200\text{pC/N}$ （定義上 $d_{31}$ は、負の値を持つ）を持ち、且つ $k_{31}$ に関する分極方向に直交する方向の横方向振動モードの共振周波数（ $f_r$ ）と素子の振動方向の長さ（ $L$ ）の積である周波数定数（ $f_c = f_r \cdot L$ ）の値 $f_c \leq 650\text{Hz} \cdot m$ であることを特徴とするドメイン制御圧電単結晶素子である。

【0010】次に、本発明の第2の発明は、分極方向の縦方向振動モードの電気機械結合係数 $k_{33} \geq 80\%$ で且つ圧電歪定数 $d_{33} \geq 800\text{pC/N}$ を持つ圧電単結晶材料において、分極方向に直交する方向の横方向振動モードの電気機械結合係数 $k_{31} \leq 30\%$ で且つ、圧電歪定数 $-d_{31} \leq 300\text{pC/N}$ （定義上 $d_{31}$ は、負の値を持つ）を持ち、且つ $k_{31}$ に関する分極方向に直交する方向の横方向振動モードの共振周波数（ $f_r$ ）と素子の振動方向の長さ（ $L$ ）の積である周波数定数（ $f_c = f_r \cdot L$ ）の値 $f_c \geq 800\text{Hz} \cdot m$ であることを特徴とするドメイン制御圧電単結晶素子である。

【0011】圧電単結晶素子は、例えば、細長比が3以上の棒状体について、その長手方向を分極方向とし、分極方向に電圧をかけた時の分極方向の振動（縦方向振動）及び歪の大きさの変換効率をそれぞれ縦方向振動モードの電気機械結合係数（ $k_{33}$ ）及び圧電歪定数（ $d_{33}$ ）で表わしており、これらの数値が大きいほど効率が良い。棒状体のほか、方形板や円板等の形状のものについてもそれそれが規定されている。本発明は分極方向に直交する方向（横方向振動モード）の電気機械結合係数（ $k_{31}$ ）に着目したドメイン制御圧電単結晶素子である。

【0012】上記第1の発明又は第2の発明に係る圧電単結晶材料としては、下記（a）又は（b）を好適に用いることができる。

【0013】（a） $X \cdot Pb(A_1, A_2, \dots, B_1, B_2 \dots)O_3 + (1-X)PbTiO_3$  ( $0 < X < 1$ ) からな

る固溶体であって、A<sub>1</sub>、A<sub>2</sub>…はZn、Mg、Ni、Lu、In及びScからなる群から選ばれた1又は複数の元素、B<sub>1</sub>、B<sub>2</sub>…はNb、Ta、Mo及びWからなる群から選ばれた1又は複数の元素で、A<sub>1</sub>、A<sub>2</sub>…のイオン価をそれぞれa<sub>1</sub>、a<sub>2</sub>…、化学式中の構成比をY<sub>1</sub>、Y<sub>2</sub>…、B<sub>1</sub>、B<sub>2</sub>…のイオン価をそれぞれb<sub>1</sub>、b<sub>2</sub>…、化学式中の構成比をZ<sub>1</sub>、Z<sub>2</sub>…とした時に、化学式Pb(A<sub>1</sub>Y<sub>1</sub>a<sub>1</sub>、A<sub>2</sub>Y<sub>2</sub>a<sub>2</sub>、…、B<sub>1</sub>Z<sub>1</sub>b<sub>1</sub>、B<sub>2</sub>Z<sub>2</sub>b<sub>2</sub>…)O<sub>3</sub>における、かっこ内の元素群のイオン価の総和WがW=a<sub>1</sub>·Y<sub>1</sub>+a<sub>2</sub>·Y<sub>2</sub>…+b<sub>1</sub>·Z<sub>1</sub>+b<sub>2</sub>·Z<sub>2</sub>…=4+の電荷を満たすこと。

【0014】(b) 上記(a)に、Mn、Cr、の1又は2種を0.5ppm~1質量%添加したものであること。

【0015】なお、最もよく知られている材料として亜鉛ニオブ酸鉛Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>やマグネシウムニオブ酸鉛Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>とチタン酸鉛PbTiO<sub>3</sub>の固溶体からなる圧電体単結晶材料(前者をPZN-Pt又はPZNT、後者をPMN-PT又はPMNTと呼称する)がある。

【0016】以上のドメイン制御圧電単結晶素子を製造する方法として次に示す製造方法がある。

【0017】その一つは、圧電単結晶素子の厚み方向の分極条件として、20°C~200°Cの温度範囲で400V/mm~1500V/mmの直流電界を最大2時間印加するか、又は電界を印加したまま冷却する(電界冷却)工程で、上記ドメイン制御圧電単結晶素子を製造することを特徴とする圧電単結晶素子の製造方法である。

【0018】この製造方法は、ドメイン制御単結晶圧電素子の最終的な分極を行う工程であるが、この工程の前段に、分極方向と直交する方向に電界を印加し、分極方向と直交する方向の強誘電体ドメインの整列状態を制御する工程を加える製造方法も有効である。分極方向と直交する方向に印加する電界の種類としては、直流電界、パルス電界、交流電界、またこれらの定常電界のほか、減衰電界などがあり、電界の強さや印加時間、温度条件等は個々の圧電単結晶素子の特性及び分極方向に直交する方向の電気機械結合係数(k<sub>31</sub>)の所望の値に応じて適正条件がある。これらは、実験等によって定めることができる。また、前記のパルス電界としては、直角波のほか、交流三角波などユニポーラ及びバイポーラパルスを用いることができる。

【0019】また、本発明の別の方法として、上記20°C~200°Cの温度範囲で400V/mm~1500V/mmの直流電界を最大2時間印加するか、又は電界を印加したまま冷却するドメイン制御単結晶圧電素子の最終的な分極を行う工程の前段に、単結晶圧電素子を加熱・冷却することを特徴とする製造方法がある。例えば、圧電単結晶素子は、菱面晶、正方晶、立方晶となる温度領域が組成に応じて決まっている。従って、例えば単結

晶圧電素子を該圧電単結晶材料の低温相である菱面晶と中温相である正方晶の転移温度を挟んで加熱冷却する工程(1)、又は該圧電単結晶材料の正方晶と強誘電性・圧電性の消失温度であるキュリー温度(この温度より高温では、該年電体単結晶材料は立方晶(高温相)となる)を挟んで加熱冷却する工程(2)、又は、高温相内で加熱冷却する工程(3)、又は、工程(1)、(2)、(3)を適宜組み合わせる工程(4)を行い、次いで20°C~200°Cの温度範囲で400V/mm~1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を行うことにより、分極方向に直交する方向の強誘電体ドメインの整列状態を制御することができる。

【0020】更に、上記20°C~200°Cの温度範囲で400V/mm~1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程ドメイン制御単結晶圧電素子の最終的な分極を行う工程の前段に、単結晶圧電素子の分極方向に直交する方向に電界を印加する工程と、単結晶圧電素子を加熱冷却する工程とを併用する工程を行い、次いで20°C~200°Cの温度範囲で400V/mm~1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を行うことにより、分極方向に直交する方向の強誘電体ドメイン整列状態を制御することができる。

【0021】

【発明の実施の形態】例えば、亜鉛ニオブ酸チタン酸鉛(PZN-PtまたはPZNT)の固溶体単結晶は、その単位格子が図1に模式的に示したようなペロブスカイト構造(ABO<sub>3</sub>)をなしている。図2にPZNとPtの組成比による相図を示した。この図はNomura et al., J. Phys. (1969)。J. Kuwata et al., Ferroelectrics (1981)より引用したものである。図2に見られるように、菱面晶PZNTでは、擬立方晶と見た時の結晶の<111>方位の8つの方向に電気双極子に相当する自発分極を有している。このような自発分極状態における<100>方向(結晶切り出し方向)に電界を印加すると、電気双極子は分極電界印加方向に回転し、自発分極方向が揃うようになる。

【0022】しかし、この揃い方には、電界の印加の様等により種々の状態が生じ、その結果、分極方向の電気機械結合係数(k<sub>33</sub>)が80%以上の値を持つにもかかわらず、分極方向に直交する方向の電気機械結合係数(k<sub>31</sub>)が、文献等によれば49~62%にばらつきを持つて分布すること、即ち、分極方向と直交する方向(横振動モード)に関して電気機械結合係数(k<sub>31</sub>)の制御がなされていないことがわかった。このようなk<sub>31</sub>の値では、積極的にk<sub>31</sub>を利用したデバイスを作製することが困難であったり、一方、積極的にk<sub>33</sub>を利用するデバイスでは分極方向の縦方向振動(k<sub>33</sub>)モード中に

スプリアスが発生したりして、十分な特性を得られない状況が発生していた。この結果を与える要因は、以下のように説明される。即ち、育成後の圧電体単結晶から切り出された圧電単結晶素子の素材では、分極方向及び分極方向と直交する方向において同一方向の電気双極子の集合からなるドメインが種々の方向を向いており、圧電性を示さず、未分極の状態にある。

【0023】一般的な分極処理温度と印加電圧を選択し、分極方向に電界を印加することにより初めて、多くのドメインが分極方向に揃っていくことができる。このことにより、分極方向の電気機械結合係数  $k_{33}$  は 80% 以上の大きな値を示すようになる。しかし、分極方向と直交する方向におけるドメインの状態は、分極方向での分極条件、即ち、分極処理温度と印加電圧の適切な範囲内でのみ制御することが可能である。

【0024】次に、分極の態様を制御する方法について、実施例をあげて説明する。表1は従来例（試料番号1, 2, 3）及び文献値（文献値1, 2）及び本発明に関する圧電単結晶材料の分極条件等を変えた場合の誘電・圧電特性を示したものである。表1中の  $d_{33}$  値は  $d_{33}$  メータ（中国科学院声学研究所製 ZJ-3D型）で測定した。 $k_{33}$  値の算出は、本発明者らの測定に基づく、図12に示す  $d_{33} vs k_{33}$  カーブから求めた。 $k_{31}$ 、 $d_{31}$ 、 $f_c$  はインピーダンスの周波数応答を測定し、計算により算出した。使用した 0.91 PZN+0.09 PT ( $X=0.91$  とモル分率で表現) の圧電単結晶素子（素子形状：13 mm長さ × 4 mm幅 × 0.36 mm厚み）を、図3に示すように6面が(100)面で囲まれた結晶10の二つの対向する(001)面に金電極をスパッタ法で作製し、40°Cのシリコンオイル中に浸漬して、電極間に 250 V/mm (試料番号4)、500 V/mm (試料番号5)、700 V/mm (試料番号6)、1000 V/mm (試料番号7)、1600 V/mm (試料番号8) の各電界を 10 分間印加した後での、 $k_{31}$  モードのインピーダンスカーブを図4～図8に示した。250 V/mm (図4) では、分極不十分の状態であり、500 V/mm (図5)、700 V/mm (図6) では、3つの  $k_{31}$  振動モードが見られるが、これは分極方向に直交する方向に複数のドメインがあるためである。

【0025】1000 V/mm (図7) では、インピーダンスカーブから明らかのように、分極方向に直交する方向でのドメインは單一ドメインとなっており、 $k_{31}$  の値は > 80% を満たすと同時に分極方向の  $k_{33}$  も > 95% を示す。1600 V/mm (図8) では、再び、2つ以上のドメインに分離し、 $k_{33}$  の値は > 95% であったが、 $k_{31}$  の値は 61% である。又、それぞれの試料の  $k_{31}$  に関する横方向振動モードの共振周波数 ( $f_r$ ) と素子の振動方向の長さ ( $L$ ) の積である周波数定数 ( $f_c = f_r \cdot L$ ) の値  $f_c$  は、試料番号4で 741 Hz

・m、試料番号5で 601 Hz · m、試料番号6で 603 Hz · m、試料番号7で 522 Hz · m、試料番号8で 700 Hz · m であった。250 V/mm、500 V/mm、1000 V/mm、1600 V/mm 印加後の分極方向に直交する面内のドメインの状態を図9に示す。

【0026】図9において、250 V/mm では分極不十分であり、500 V/mm では複数ドメイン（マルチドメイン）であるが、 $k_{31}$  に関わる分極成分の相乗作用で  $k_{31}$  が大きくなる。1000 V/mm では單一ドメインとなり、さらに 1600 V/mm では複数ドメインとなり、 $k_{31}$  に関わる分極成分の相殺作用で  $k_{31}$  が小さくなる。本発明内で高  $k_{33}$  ( $d_{33}$ )、高  $k_{31}$  ( $d_{31}$ ) が得られるドメイン配列は 500 V/mm、1000 V/mm であった。一方、同様な設定の素子、試料番号9を 200°C のシリコンオイル中で、400 V/mm の直流電界を印加したまま、シリコンオイルの温度を室温まで降下させると、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  は ≥ 80% であり、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  は > 70% であった。この時の  $f_c$  は 609 Hz · m であった。試料番号10では、同じ設定の素子を 60°C のシリコンオイル中に浸漬し、400 V/mm の直流電界を 120 分間印加した。その結果、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  は > 95% であったが、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  は < 30% であった。

【0027】又、試料番号11では、同じ設定の素子に 1500 V/mm の直流電界を 10 分間印加すると、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  は > 90% であったが、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  は < 30% であった。試料番号10及び試料番号11の  $f_c$  は、それぞれ 981 Hz · m 及び 1004 Hz · m であった。この結果は、横方向振動を抑えるドメイン配列からくるものと考えられる。

【0028】このように分極条件（印加電圧、温度等）を適切に設定することにより、分極時のドメイン状態及び、それに依存する  $k_{33}$ 、 $k_{31}$  の値を制御することができる。又、ここに示した実施例に限らず、20°C～200°C の温度範囲で 400 V/mm～1500 V/mm の直流電界を最大 2 時間印加するか又は電界を印加したまま冷却する工程の温度範囲、分極電界値範囲、印加時間範囲と印加方法を用いることにより、上記案施例にと同様な誘電・圧電特性が得られることが確認されている。

【0029】更に、20°C～200°C の温度範囲で 400 V/mm～1500 V/mm の直流電界を最大 2 時間印加するか又は電界を印加したまま冷却する工程に関しては、キュリー温度以上の 200°C で 1 時間保持する脱分極の工程を挟んで、20°C～200°C の温度範囲で 4

00V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の工程を繰り返すことによって第1の発明、第2の発明に示す特性が向上することが確認されている。これらの結果を、分極方向に直交する方向（横方向振動モード）の電気機械結合係数k31とk31モードの共振周波数（fr）と素子の振動方向の長さ（L）の積である周波数定数（fc31=fr・L）の値で整理すると図10に示すような高k33、高k31の領域と高k33、低k31の領域が周波数定数（fc31=fr・L）の値の範囲を横軸として得られることが解った。

【0030】従来例及び文献値も同時に図10に記載したが、従来例及び文献値ではk31モードの共振周波数（fr）と素子の振動方向の長さ（L）の積である周波数定数（fc31=fr・L）の値が本発明の請求項1、2の中間にあり、本発明で明らかにしたように分極方向と直交する方向のドメイン制御が不充分な領域にあり、そのため、k31の値がばらつくものと考えられる。

【0031】次に、単結晶圧電素子の分極方向に直交する方向に電界を印加し、分極方向に直交する方向の強誘電体ドメインの方向を制御する工程、単結晶圧電素子を該圧電単結晶材料の低温相である菱面晶と中温相である正方晶の転移温度を挟んで加熱冷却する工程（1）、又は該圧電単結晶材料の正方晶と強誘電性・圧電性の消失温度であるキュリー温度を挟んで加熱冷却する工程

（2）、又は、高温相内で加熱冷却する工程（3）、又は、前記工程（1）、（2）、（3）を適宜組み合わせた工程（4）を行い、次いで20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を行った実施例について表2に則して説明する。表2中のd33の測定、k33値の算出、k31、d31、fc31の測定及び計算は表1と同様である。

【0032】試料番号12では、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の工程の前に、上記の単結晶圧電体素子と同じ形状の素子に、図11に示すように図3の（001）面11と直交して対向する2つの（010）面13に金電極をスパッタ法で作製し、40°Cのシリコンオイル中で1000V/mmの直流電界を10分間印加し分極した。素子を取り出したあと、エッティング液で該金電極を除去し、更に図3に示す二つの対向する（001）面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。

【0033】その結果、表2の試料番号12に示すように、分極方向（縦方向振動モード）の電気機械結合係数

k33で97.3%、圧電歪定数d33で2810pC/Nを得た。又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数k31で85.5%、圧電歪定数d31で-2380pC/Nを得た。k31に関する横方向振動モードの共振周波数（fr）と素子の振動方向の長さ（L）の積である周波数定数（fc31=fr・L）の値fc31は、483Hz・mであった。

【0034】試料番号13、14、15では、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の前に、上記の単結晶圧電体素子と同じ形状の素子を、それぞれシリコンオイル中に浸漬し、50～90°C、150～200°Cの温度範囲を、更に温度槽内で200～400°Cの温度範囲を30分周期で3回温度上昇・下降を繰り返した。その後、図3に示す二つの対向する（001）面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。その結果、試料番号13では、分極方向（縦方向振動モード）の電気機械結合係数k33で97.5%、圧電歪定数d33で2840pC/Nを得た。

【0035】又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数k31で85.3%、圧電歪定数d31で-2360pC/Nを、試料番号14では分極方向（縦方向振動モード）の電気機械結合係数k33で97.8%、圧電歪定数d33で2880pC/Nを得た。

【0036】又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数k31で85.3%、圧電歪定数d31で-2350pC/Nを、試料番号15では、分極方向（縦方向振動モード）の電気機械結合係数k33で97.4%、圧電歪定数d33で2820pC/Nを得た。又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数k31で85.6%、圧電歪定数d31で-2380pC/Nをそれぞれ得た。周波数定数（fc31=fr・L）の値fc31は、試料番号13では、503Hz・m、試料番号14では、506Hz・m、試料番号15では、437Hz・mmであった。

【0037】試料番号16では、図11に示すように図3の（001）面11と直交して対向する2つの（010）面13に金電極をスパッタ法で作製し、シリコンオイル中に浸漬し、150～200°Cの温度範囲を30分周期で3回温度上昇・下降を繰り返しながら、直流電界400V/mmを印加した。素子を取り出したあと、エッティング液で該金電極を除去し、更に図3に示す二つの対向する（001）面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2

時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。その結果、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.8%、圧電歪定数  $d_{33}$  で 2870 pC/N を得た。又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 86.0%、圧電歪定数  $d_{31}$  で -2450 pC/N を得た。周波数定数 ( $f_{c31} = f_r \cdot L$ ) の値  $f_{c31}$  は、415 Hz · m であった。

【0038】尚、図3の(001)面と直交して対向する別の面として、図11の(100)面間に直流電界を印加後、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施しても、同じ効果が得られることを確認している。

【0039】試料番号17では、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の前に、上記の単結晶圧電体素子と同じ形状の素子に、図11に示すように図3の(001)面11と直交して対向する2つの(010)面13に金電極をスパッタでつけ、60°Cのシリコンオイル中でピーク値500V/mm、周期800msのバイポーラ三角波電界を10分間印加した。バイポーラ三角波の波形を図3に示した。素子を取り出したあと、エッティング液で該金電極を除去し、更に図3に示す二つの対向する(001)面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。その結果、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.1%、圧電歪定数  $d_{33}$  で 2780 pC/N を得た。又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 18.3%、圧電歪定数  $d_{31}$  で -230 pC/N を得た。周波数定数 ( $f_{c31} = f_r \cdot L$ ) の値  $f_{c31}$  は、863 Hz · m であった。

【0040】試料番号18、19、20では、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の前に、上記の単結晶圧電体素子と同じ形状の素子を、それぞれシリコンオイル中に浸漬し、50～90°C、150～200°C、200～400°Cの温度範囲を5分周期で3回温度上昇・下降を繰り返した。その後、図3に示す二つの対向する(001)面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。

【0041】その結果、試料番号18では、分極方向

（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.0%、圧電歪定数  $d_{33}$  で 2760 pC/N を、又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 18.6%、圧電歪定数  $d_{31}$  で -260 pC/N を得た。試料番号19では、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.3%、圧電歪定数  $d_{33}$  で 2810 pC/N を、又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 17.8%、圧電歪定数  $d_{31}$  で -190 pC/N を得た。

【0042】試料番号20では、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.2%、圧電歪定数  $d_{33}$  で 2790 pC/N を、又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 18.2%、圧電歪定数  $d_{31}$  で -220 pC/N をそれぞれ得た。周波数定数 ( $f_{c31} = f_r \cdot L$ ) の値  $f_{c31}$  は、試料番号18では、836 Hz · m、試料番号19では、892 Hz · m、試料番号20では、847 Hz · m であった。

【0043】試料番号21では、図11に示すように図3の(001)面11と直交して対向する2つの(010)面13に金電極をスパッタ法で作製し、シリコンオイル中に浸漬し、150～200°Cの温度範囲を5分周期で3回温度上昇・下降を繰り返しながら、直流電界400V/mmを印加した。素子を取り出したあと、エッティング液で該金電極を除去し、更に図3に示す二つの対向する(001)面11に金電極をスパッタ法で作製し、上記実施例で示した20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程を実施し、誘電・圧電特性を測定した。その結果、分極方向（縦方向振動モード）の電気機械結合係数  $k_{33}$  で 97.7%、圧電歪定数  $d_{33}$  で 2850 pC/N を得た。又、分極方向に直交する方向（横方向振動モード）の電気機械結合係数  $k_{31}$  で 17.6%、圧電歪定数  $d_{31}$  で -150 pC/N を得た。周波数定数 ( $f_{c31} = f_r \cdot L$ ) の値  $f_{c31}$  は、924 Hz · m であった。

【0044】上記ドメイン制御圧電単結晶素子に際し、最終的な分極を行う工程、即ち、20°C～200°Cの温度範囲で400V/mm～1500V/mmの直流電界を最大2時間印加するか又は電界を印加したまま冷却する工程の前段に、分極方向と直交する方向に電界を印加し、分極方向と直交する方向の強誘電体ドメインの整列状態を制御する方法、圧電単結晶材料の低温相である菱面晶と中温相である正方晶の転移温度を挟んで加熱冷却する工程（1）、又は圧電単結晶材料の正方晶と強誘電性・圧電性の消失温度であるキュリー温度（この温度より高温では、該圧電体単結晶材料は立方晶（高温相）となる）を挟んで加熱冷却する工程（2）、又は、高温相内で加熱冷却する工程（3）、又は、工程（1）、

(2)、(3)を適宜組み合わせた工程(4)により分極方向と直交する方向の強誘電体ドメインの整列状態を制御する方法、単結晶圧電素子の分極方向に直交する方向に電界を印加する工程と、単結晶圧電素子を加熱冷却する工程とを併用する工程により分極方向と直交する方向の強誘電体ドメインの整列状態を制御する方法を実施することは、結晶育成時の徐冷過程で生成される結晶中の複数のドメインを、上記の各工程を実施することにより、より人の制御されたものとし、上記ドメイン制御圧電単結晶素子を製造するドメイン制御単結晶圧電素子の最終的な分極を行う工程での分極方向に直交する方向のドメイン構造を、より容易に制御するために有効であること、又、本発明の第1の発明、第2の発明でいう誘電・圧電特性を向上させるために有効であることがわかった。

## 【0045】

試料番号	分極条件			誘電・圧電特性					適用される請求項等
	温度 ℃	電界E V/mm	時間 min	k <sub>33</sub> %	d <sub>33</sub> 10 <sup>-12</sup> C/N	k <sub>31</sub> %	d <sub>31</sub> 10 <sup>-12</sup> C/N	f <sub>c<sub>31</sub></sub> Hz · m	
1	20	1800	10	95.6	2550	61.5	-970	701	従来例
2	60	400	150	95.3	2500	48.7	-694	773	従来例
3	100	300	120	94.0	2360	35.0	-520	755	従来例
4	40	250	10	56.0	165	18.9	-224	741	分極不十分
5	40	500	10	84.0	1190	76.0	-1310	601	請求項1
6	40	700	10	87.0	1420	77.1	-1324	603	請求項1
7	40	1000	10	95.3	2500	80.8	-1701	522	請求項1
8	40	1600	10	95.3	2500	60.9	-939	700	請求項1
9	200	400	電界冷却	80.2	960	74.7	-1263	609	請求項1
10	60	400	120	96.9	2740	26.3	-288	981	請求項2
11	20	1500	10	94.6	2300	27.1	-291	1004	請求項2
文献値1				94	2300	53	-1100	-	
文献値2				90	1734	49	-962	680-733 (平均値: 707)	

## 【0047】

【表2】

試料番号	処理内容	条件	誘電・圧電特性					対応する請求項
			k <sub>33</sub> %	d <sub>33</sub> 10 <sup>-12</sup> C/N	k <sub>31</sub> %	d <sub>31</sub> 10 <sup>-12</sup> C/N	f <sub>c<sub>31</sub></sub> Hz · m	
12	請求項5	直流電界 1000V/mm、40°C、10分	97.3	2810	85.5	-2380	483	請求項1
13	請求項6	50~90°C、30分周期、繰り返し3回	97.5	2840	85.3	-2360	503	請求項1
14	請求項6	150~200°C、30分周期、繰り返し3回	97.8	2880	85.3	-2350	506	請求項1
15	請求項6	200~400°C、30分周期、繰り返し3回	97.4	2820	85.6	-2380	437	請求項1
16	請求項7	直流電界 400V/mm、150~200°C、30分周期、繰り返し3回	97.8	2870	86.0	-2450	415	請求項1
17	請求項5	バイポーラ三角波 500V/mm、周期 800ms、10分	97.1	2780	18.3	-230	863	請求項2
18	請求項6	50~90°C、5分周期、繰り返し3回	97.0	2760	18.6	-260	836	請求項2
19	請求項6	150~200°C、5分周期、繰り返し3回	97.3	2810	17.8	-190	892	請求項2
20	請求項6	200~400°C、5分周期、繰り返し3回	97.2	2790	18.2	-220	847	請求項2
21	請求項7	直流電界 400V/mm、150~200°C、5分周期、繰り返し3回	97.7	2850	17.6	-150	924	請求項2

## 【図面の簡単な説明】

【図1】結晶構造の模式的斜視図である。

【図2】PZN-PT (PZNT) の相図である。

## 【図3】電界印加の説明図である。

【図4】k<sub>31</sub>振動モードのインピーダンスカーブの図である。

【図5】 $k_{31}$ 振動モードのインピーダンスカーブの図である。

【図6】 $k_{31}$ 振動モードのインピーダンスカーブの図である。

【図7】 $k_{31}$ 振動モードのインピーダンスカーブの図である。

【図8】 $k_{31}$ 振動モードのインピーダンスカーブの図である。

【図9】電界印加後の分極方向（厚み方向）面内のドメインの状態の図である。

【図10】電気機械結合係数 $k_{31}$ と $k_{31}$ 振動モードの共

振周波数 ( $f_r$ ) と素子の振動方向の長さ ( $L$ ) の積である周波数定数 ( $f_c = f_r \cdot L$ ) の値のグラフである。

【図11】電界印加の説明図である。

【図12】 $k_{33}$ 対 $d_{33}$ のグラフである。

【図13】バイポーラ三角波パルスの波形図である。

【符号の説明】

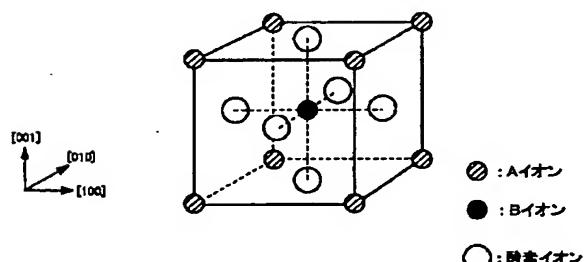
10 圧電単結晶素子

11 電極面 (001)

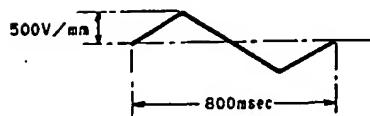
12 電界

13 電極面 (010)

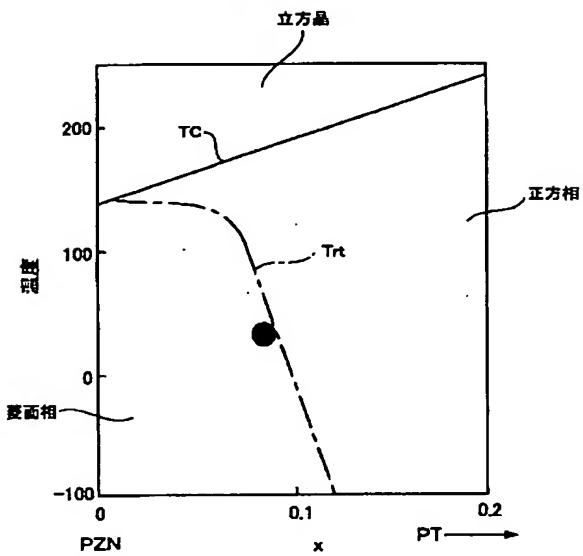
【図1】



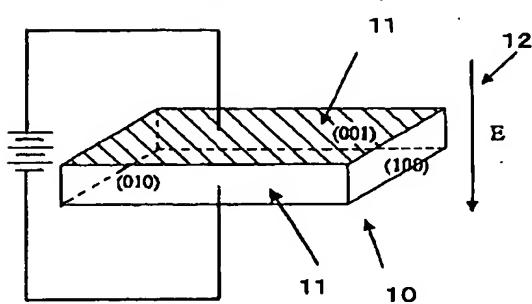
【図13】



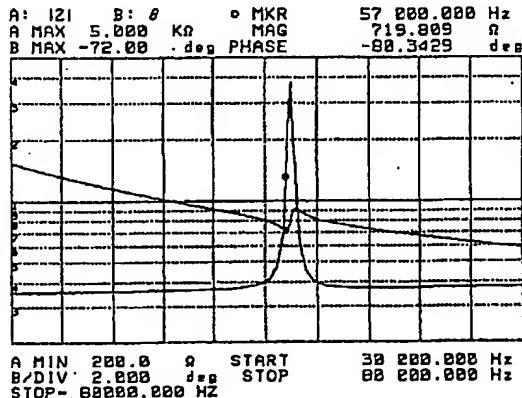
【図2】



【図3】

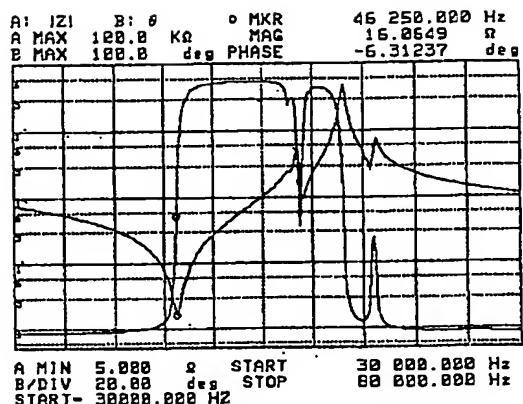


【図4】



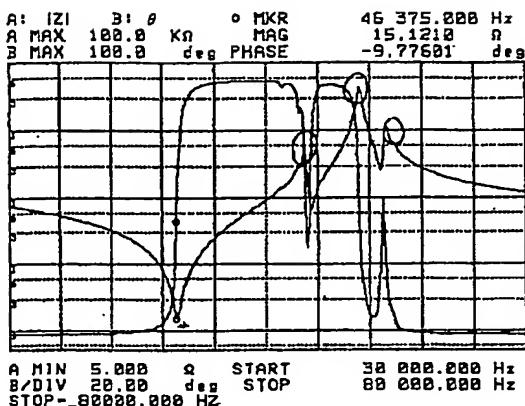
250V/mm

【図5】



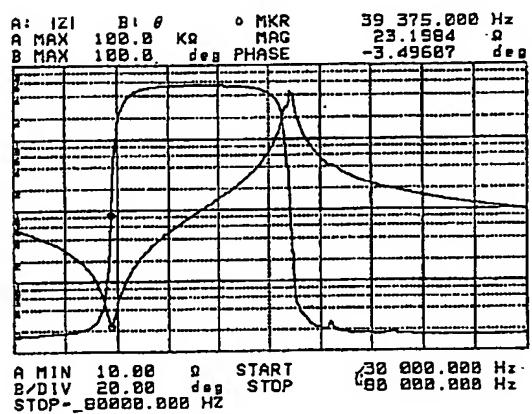
500V/mm

【図6】



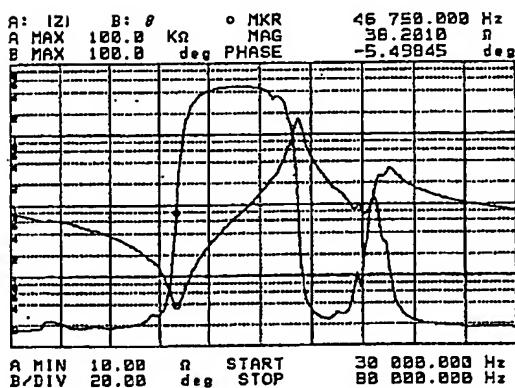
700V/mm

【図7】



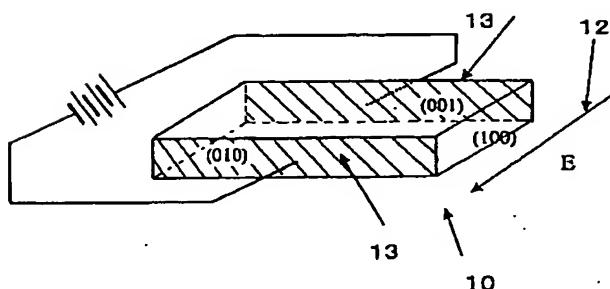
1000V/mm

【図8】

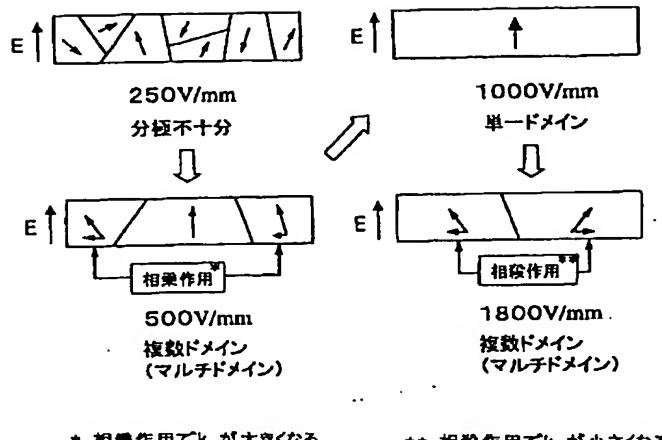


1600 V/mm

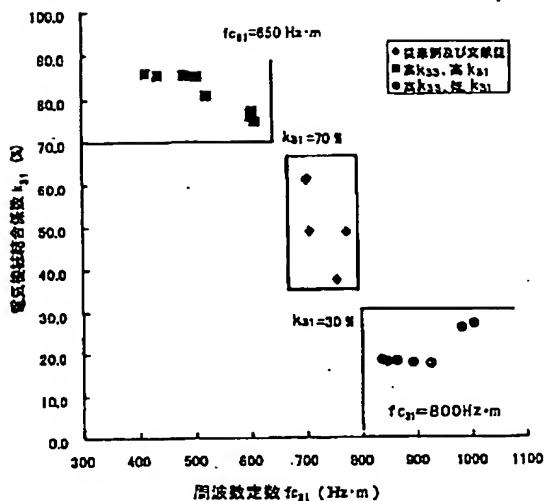
【図11】



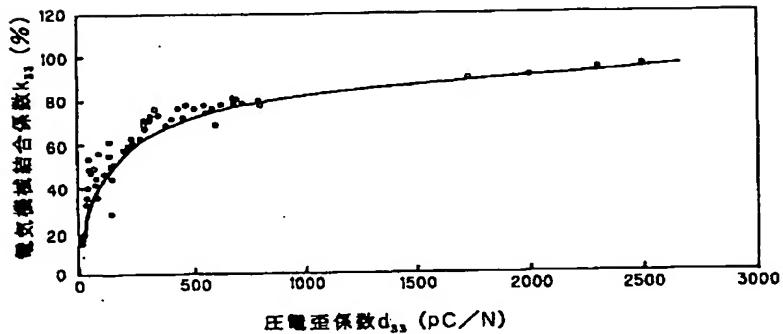
【図9】



【図10】



【図12】



フロントページの続き

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